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INTEGRATED PROCESS FOR SEPARATION OF OIL, PROTEIN, CARBOHYDRATES, SHELL AND MINOR TOXIC COMPONENTS FROM SEEDS

Technical Field of the Invention

This invention relates to the separation of components in cottonseeds, rubber seeds, and other seeds into oil, protein, carbohydrates, shell and toxic components.

Background of the Invention

The separation of oils and fats from vegetable materials had constituted a distinct and specialized branch of fat technology. Most of all the extraction processes have common objectives: to obtain the oil uninjured and as free as possible from undesirable impurities, secondly, to obtain the oil in as high a yield as is consistent with the economy of the process and lastly, to produce residue or co-product of the greatest value.

In the case of seed or other materials initially high in oil and low in solids content, the unextracted residue will contain only a small fraction of the total oil; however in seeds of low solid content, such as soybeans, it may contain as much as 15-20% of the total oil. In the processing of cottonseed, special attention had to be given to the inactivation of gossypol or other toxic constituents.

Historically, the extraction of cottonseed oil has not been able to achieve the best yield that is consistent with the economy of the process. For example, the average yield of oil from the commercial processing of cottonseed by solvent extraction and using undecorticated seeds is 18%. Cottonseed oil that is extracted by conventional technology is brownish yellow and contains the toxic substance gossypol, hence it is not popular to consumers. Cottonseed residue (pulp) is used as feedstuff for oxen and sheep or used as fertilizer.

A need arises for a new effective method and apparatus for gossypol extraction from cottonseed kernel, converting wastes into valuables, and to extract innoxious high-grade cotton oil, protein and oligosaccharides. At the same time, this new technology does not involve discharge of wastewater and offscum, therefore, overcoming environmental pollution as in the conventional processes.

In this preferred embodiment, cottonseed is discussed but examples of other suitable seeds such as sunflower seed; safflower, peanuts, flax seed, hemp seed, rape seed, poppy seed and rubber seed can be used.

Summary of the Invention

It is therefore an object of this invention to provide a process for separation of oil, protein, carbohydrates, shell and minor toxic components from seeds.

It is yet another object of the invention to provide for a seed oil obtained by the method according to the present invention.

It is a further object of the invention to provide for an apparatus to produce a seed oil according to the method of the present invention.

Accordingly, there is provided a process for separation of oil, protein, carbohydrates, shell and minor toxic components from oil seed wherein said process comprises the steps of:

a. dehulling of oil seed to separate out the shell and kernel;
b. compressing the kernel obtained in (a) into flakes at room temperature;
c. agitating and mixing the flakes obtained in (b) with a mixture of dephenolizers comprising alcohol, acid and an enzyme, for a period of time at a specific temperature;
d. mixing the filtrate obtained in (c) with a complexing compound to form a gossypol complex;
e. hydrolyzing, crystallizing, filtering and washing the gossypol complex to yield industrial gossypol;

f. treating the dephenolized flakes obtained in (c) with liquid propane and butane to yield oil, for a period of time at a specific temperature;

g. dissolving pulp derived from oil extraction in alkali to yield protein upon precipitation; and

h. adding saturated limewater to protein waste solution obtained in (g), followed by precipitation, filtration of residual gossypol, electrolysis and condensation to yield carbohydrates.

A process of separating gossypol includes the decorticated and dehulling of delintioned cottonseed to separate the cottonseed shells and kernels, the cotton seed kernel obtained will be compressed into flakes whereby the shells goes through a dephenolization process to form melanin.

The compressed flakes is agitated and mixed with dephenolizers. This mixture will then be leached for a known period of time and transferred to a complexing tank. The addition of aniline to form aniline-gossypol complex, goes through hydrolyzation, crystallization, filtration and lastly washing to yield industrial gossypol.

The dephenolized cottonseed kernels are immersed with a mixture of propane and butane to extract the oil. The oil is recycled through decompression, aeration and evaporation to form clear cotton oil. The residue (pulp) from which oil has been extracted is dissolved via an alkaline treatment before being purified through centrifugation. The pH of the supernatant is then adjusted with acid to a lower pH and further centrifuged. The protein precipitation on the other hand is bleached and spray-dried to obtain cotton protein powder.

The protein waste solution is then added with saturated limewater, precipitated, filtration of residual gossypol, electrodialysis and condensed to form paste-like cottonseed sugar.

Apparatus for the extraction of gossypol sugar from cottonseed includes the means of treating the husked cottonseed kernels with a mixture of dephenolizers includes alcohol, acid and enzyme. The present invention also describes a method of complexing with compounds such as aniline to produce aniline-gossypol complex, which then yields industrial gossypol.. Also mentioned are the means of extracting oil from the dephenolized cotton seed kernel that is in propane and butane solutions. The invention also describes the means of treating cottonseed residue (pulp) with alkaline solution and dissolving it, followed by centrifugation for purification, and adding of acid and further centrifugation. The present invention also includes the means of hydrolyzation and the addition of enzyme compound to acquire hydrolyzed protein. Also described are the means of adding saturated limewater to protein wastewater solution and condensing it to obtain a paste-like cottonseed sugar.

The present invention has many advantages. In general, it is an integrated process to separate oil, protein, carbohydrates, shell and minor toxic components from cotton seed. Although cottonseed is preferred, other suitable oil seeds can be used.

Brief Description of the Figures

Figure 1 is a flow chart showing the process of separation of oil, protein, carbohydrates, shell and minor toxic components from oil seed.

Figure 2 is a schematic diagram showing the oligosaccharide plant of the present invention.

Figure 3 is a schematic diagram showing the integrated process of separation of oil, protein and minor toxic components from oil seed of the present invention.

Detailed Description of the Figures

Figure 1 shows the steps in the process of oil extraction from oil seed, including extraction of oligosaccharides and protein of the present invention.

Figure 2 shows the alkali refining and oligosaccharide plants of the present invention. In the alkali refining plant, the separator/skimming tank is denoted by (1), the alkali refining tank by (2), the flushing separator by (3), the saponification tank by (4) and the acid flushing tank by (5). Referring to the oligosaccharide plant, the dehydration filtration apparatus is represented by (1), the dessicator by (2), the separator by (3), the condenser by (4) and the crystal separator by (5).

Figure 3 shows the integrated process for oil extraction comprising the husking, oil fraction, protein separation and gossypol plants of the present invention. In the husking plant, the cottonseed husking machine is denoted by (1) and the flaking machine by (2). The oil fraction plant comprises of gas propelled valve (1), vacuum pump (2), compressor (3), oil fraction tank (4), buffer tank (5), condenser (6), residue (pulp) dissolving tank (7), raw oil temporary storage tank (8), evaporator (9), solvent tank (10) and separator (11). The protein separation plant consists of the neutralization, disinfecting and antibacterial tank (1), separator (2,3), spray dryer (4) and dryer (5). Referring to the gossypol plant, the plant comprises of a water outlet (1), a water inlet (2), connection to vacuum pump (3), vapour inlet ((4), dihronate (5), crystallization tank (6), oil filtration tank (7), hydrolyzation tank (8), vacuum buffer (9), evaporator (10), condenser (11), methanol temporary storage tank (12), vacuum dryer (13) and separator (14).

Detailed Description of the Invention

The present invention, either as steps of the invention or as combinations of parts of the invention, will now be more particularly described in this section. It will be understood that the particular embodiments of this invention are shown by way of illustrations and not as limitations of the invention. The principal features of the invention may be employed in various embodiments without departing from the scope of the invention.

In this invention, cottonseed is the preferred embodiment. Therefore the characteristics and history of cottonseed is disclosed as follows: Cottonseed kernel contain 26% oil and more than 36% protein. Principally, fatty acid in cotton oil

contains oleic acid, linoleic acid and other unsaturated fatty acid group, as well as rich in nutritional ingredients such as –OH containing compounds. It has high physiological value. Cottonseed residue (pulp) after defatting is as high as 45% and more, with its main amino acid composition better than soybean protein. Cottonseed kernel is also rich in cottonseed sugar and other oligosaccharides.

Even though gossypol is a toxic substance, it is also an important raw material for chemical industry.

The process to achieve the above mentioned is described below and one of the embodiments of the present invention, integrated process is shown in Figure 3. Cottonseed is directed into the cottonseed husking machine (1) in the husking plant. Other suitable oil seeds such as sunflower seed, safflower seed, rape seed, poppy seed and flax seed can be used.

The first step in the processing of oil seeds is cleaning to separate foreign materials. Sticks, stems, leaves, and similar trash are usually removed by means of revolving screens or reels. Sand and dirt is also removed by screening. Other equipment such as permanent electromagnets installed on conveyor belts, special "stoners" or pneumatic system are used. The cleaning of oil seeds is preferably carried out before the seeds are placed in storage.

One embodiment of the present invention, integrated process system is shown in Figure 3. Oil seeds are preferably decorticated before they are separated. The hulls of oil-bearing seeds are low in oil content, usually containing not more than about 1%. If the hulls are not removed from the seeds before the kernel is extracted, they reduce the total yield of oil by absorbing and retaining oil in the residue and hence reduce the capacity of the extraction equipment.

The hulling machine used for decortication of medium-sized oil seeds with a flexible seed coat, such as cottonseed, peanuts and sunflower seed are of two principal types: bar hullers and disc hullers.

The rotating member of a bar huller is a cylinder equipped on its outer surface with a slightly projecting, longitudinally placed, sharply ground, square-edged knives or " bars". The seeds are fed between the rotating cylinder and the concave member, and the hulls are split as the seeds are caught between the opposed cutting edges. The disc huller on the other hand is more or less similar in principle to the bar huller, except that the cutting edges consist of grooves cut radially in the surfaces of two opposed and vertically mounted discs, one of which is stationary and the other rotating. The condition of the seed is somewhat critical. In the case of cottonseed the following separations are commonly carried out: (a) separation of large meat particles from hulls and uncut seed by screening; (b) separation of hulls from uncut seed by air lift; (c) separations of small meat particles from hulls by beating and screening and (d) separation of hull particles from meats by air.

In this embodiment, cottonseeds are invariably delivered to the mills from the gins without removal of the coating of short fibers or linters and must be delinted before they are hulled. Delintering machines (known as linters) are similar in principle and appearance to cotton gins, consisting essentially of a revolving assembly of closely spaced circular saws that pick the lint from the seed. The fibers are removed from the saw teeth by revolving cylindrical brush or by air blast that suspends them in an air stream in which they are conveyed through pipes to collection equipment.

In this invention, after the dehulling of cottonseed, through rigid separation of shells and kernels, cottonseed kernel is compressed into a 0.28 – 0.35 millimeters flakes at room temperature using flaking machine vessel 2 in Figure 3. The compressed flakes will facilitate the extraction process by reducing the distances that solvent and oil must diffuse in and out of the seed during the extraction process. The extraction rate should theoretically be indirectly proportional to the square of the flake thickness; doubling the thickness, for example, should quadruple the time required for reduction of the residual oil to a given level. Reasonably high moisture content is required in oil seeds that are to be formed into thin, coherent flakes. Very dry flakes do not flake well.

These flakes are fed into an agitated leaching (extraction) tank (4) in the immersion plant. In this vessel the flakes are agitated and mixed with a mixture of dephenolizers, which contain methanol (or ethanol), phosphoric acid (nitric acid, etc.) and enzymes. In this preferred embodiment, the time to leach the flakes and dephenolizers is between the ranges of 15 minutes to 18 hours. The preferred temperature used ranges from 0°C to 70°C.

In order to fully extract the gossypol in the cottonseed kernels, especially to convert the gossypol-complex into free gossypol by de-bonding, without denaturing the cotton proteins and to minimize usage of soluble oil in the process of dephenolization, this technology has included the dephenolization mixture. In a preferred embodiment, it consists of methanol (ethanol), nitric acid (hydrochloric acid or phosphoric acid, etc.) and enzymes at concentrations respectively of 65 – 99%, 3 - 85%, 0.4 – 65ug/ml and weight ratio of 10 – 15.0 : 0.005-0.05 : 0.00006 – 0.0009. The weight ratio of dephenolization mixture to cottonseed kernel is 3 – 15 : 1. Other ratios are dependent of the types of oil seeds used.

In a preferred embodiment, the filtrate is transferred into a complexing tank vessel where the compound aniline is added to produce aniline-gossypol complex, through hydrolyzation that takes place in the hydrolyzation tank (8) in the gossypol plant. Other compounds such as chromium, if added, will form chromium - gossypol complex. The formed complex will undergo crystallization in the crystallization tank (6), filtration in the oil filtration tank (7), and later washing, which yields more than 80% of industrial gossypol.

The remaining solution is transferred into the separator (3) in the oligosaccharide plant. In this embodiment, dephenolized cottonseed kernel, with the addition of propane and butane, is immersed in the immersion tank (4) in the immersion plant to extract out the oil at 5°C to 45°C. The extracted oil mixture can be recycled to obtain clear innoxious cotton oil, through decompression, aeration and evaporation in propane and butane solutions. Cottonseeds residue (pulp) which oil has been extracted, is transferred into the protein extraction tank vessel.

Alkali (either NaOH or KOH) is added to adjust the pH value to between 9 and 12. It is dissolved in the alkaline solution for 10 - 90 minutes, followed by centrifugation for separation (purification). The supernatant is added with acid to adjust the pH value to 3.8 to 5.8 and further centrifuged. Its protein precipitation is bleached and sent to the spray-drying tower to obtain separated cotton protein powder. After the centrifugation process and prior to the spraying process, it is then sent for hydrolyzation and addition of proteolytic enzyme compound for enzymolysis. Hydrolyzed protein is obtained. Protein waste (water) solution and waste (water) solution from hydrolyzation of gossypol-complex are transferred into the oligosaccharide evaporating tank, evaporated and filtered to get smaller molecule ethanol, and water soluble protein. Saturated limewater is added and the mixture is allowed to precipitate. This is followed by filtration of the residual gossypol and removal of salt by electrodialysis, its residual solution is condensed to get paste-like cottonseed sugar.

In order to ensure the cotton protein is stable (does not denature) and to minimize residual solution, this preferred embodiment had adopted a non – CO_2 supercritical extraction method to obtain oil and to flush away residual dephenolizer (dephenolization mixture) in the cotton seed cake (extracted pulp). A supercritical fluid is a material, which can be either liquid or gas, used in a state above the critical temperature and critical pressure where gases and liquids can coexist. It shows unique properties that are different from those of either gases or liquids under standard conditions. This preferred supercritical fluid has either both the gaseous property of being able to penetrate anything, or the liquid property of being able to dissolve materials into their components. In this one preferred embodiment, such solution used is a mixture of propane and butane.

Supercritical fluids offer a favorable means to achieve solvating properties that have gas- and liquid-like characteristics without actually changing its chemical structure. By proper control of pressure and temperature, a significant range of physiochemical properties (density, diffusivity, dielectric constants, etc.) without passing through a phase boundary, e.g. changing from gas to liquid form. In one

embodiment, its working pressure is 0.6 mpa – 1.2 mpa and the temperature ranges from 0°C to 35°C. The ratio of both gasses preferred 1- 6:9 - 4. The weight ratio of this mixture to cottonseed accordance to this invention is 2 – 17 : 1. The weight ratio between propane/butane and cotton kernel is 0.5 – 9 : 1. The extraction time ranges from 10 minutes to 8 hours.

Supercritical extraction provides some distinct advantages over other separation techniques: thermally unstable compounds can be separated at low temperatures; the solvent can be removed easily from the solute by reducing the pressure and/or adjusting the temperature; thermal energy requirements are lower that for distillation; surprisingly high selectivity for the solute can be accomplished; rapid extraction can be achieved due to low viscosity, high diffusivity and good solvating power of the supercritical fluid solvent.

This technology of extracting and refining gossypol from cottonseed is more convenient than conventional technologies at lower cost. The transferring cost is lowered because of its direct hydrolysis of diphenylamine gossypol under acid and antioxidant conditions. Its content of acids (sulphuric acid, hydrochloric acid, nitric acid etc.) concentration is 8 - 49%, content of antioxidant is 50 - 99%, content of acetone is 20 - 95%. Chromium-gossypol complex hydrolyzation additive is formed at the weight ratio of 5 – 15 : 1 – 7 : 11 - 45. Its weight ratio with diphenylamine is 11 - 25 : 3 - 16. Other industrial seeds can be used.

This invention has overcome the shortcoming of conventional protein factories which pollute the environment with organic waste water, and it produces oligosaccharide supplement by evaporation, dephenolization, removal of salt and condensation of the gossypol waste water and protein waste water. The evaporation temperature during production is 70°C to 200°C. Evaporation time ranges from 10 minutes to 90 minutes.

In one embodiment, the pH value limewater used to remove phenol is 8.5 - 12 and its weight ratio to waste water is 0.05 - 0.7 : 1.

While particular embodiments of the subject invention have been described, it will be obvious to those skilled in the art that various changes and modifications to the subject invention can be made without departing from the spirit and scope of the invention. It is intended to cover, in the appended claims, all such modifications that are within the scope of this invention.

Claims:

1. A process for extracting oil, protein, carbohydrates, shell and minor toxic components from seeds comprising:
    a. dehulling of oil seed to separate out the shell and kernel;
    b. compressing the kernel obtained in (a) into flakes at room temperature;
    c. agitating and mixing the flakes obtained in (b) with a mixture of dephenolizers comprising alcohol, acid and enzyme, for a period of time at a specific temperature;
    d. mixing the filtrate obtained in (c) with a complexing compound to form a gossypol complex;
    e. hydrolyzing, crystallizing, filtering and washing the gossypol complex to yield industrial gossypol;
    f. treating the dephenolized kernel flakes obtained in (c) with liquid propane and butane to yield oil, for a period of time at a specific temperature;
    g. dissolving pulp derived from oil extraction in alkali to yield protein upon precipitation; and
    h. adding saturated limewater to protein waste solution obtained in (g), followed by precipitation, filtration of residual gossypol, electrolysis and condensation to yield carbohydrates.

2. A process of claim 1, wherein the oil seed kernel is directly flaked or cold pressed.

3. A process of claim 1 or 2, wherein the dephenolization mixture comprises an alcohol such as methanol or ethanol, an acid such as nitric acid, hydrochloric acid, phosphoric acid or any other suitable acid, and an enzyme.

4. A process of claim 3, wherein the alcohol concentration is from 65%-99%, the acid concentration is from 3%-85%, and the enzyme concentration is from 0.4 - 65ug/ml.

5. A process of claim 3 or 4, wherein the specific gravity of alcohol : acid : enzyme is 10 – 15 : 0.005 - 0.05 : 0.00006 - 0.009.

6. A process of any one of claims 3, 4 or 5, wherein the ratio of dephenolization mixture to oil seed kernel is 3 – 5 : 1, dephenolization time is 15 minutes to 18 hours and the temperature is 0^{o} - 70^{o}C.

7. A process of claim 1, wherein the complexing compound is aniline, chromium or any other suitable complexing compound.

8. A process of claim 1, wherein the weight ratio of liquid propane and butane to oil seed kernel is 0.5 – 9 : 1 and the elution time is 10 minutes to 8 hours.

9. A process of claim 1 further comprising the step of separating gossypol from seed, wherein the seed oil-complex hydrolyzation additive comprises sulphuric acid or nitric acid or any other suitable acid, antioxidant and acetone with weight ratio of 5 – 15 : 1 – 7 : 11 - 45 respectively.

10. A process of claim 9, wherein the weight ratio of the hydrolyzation additive and seed oil-complex is 11 – 25 : 3 - 16.

11. A process of claim 1 further comprising the step of forming aniline-gossypol complex that is subjected to hydrolyzation, crystallization, filtration and washing to yield industrial gossypol.

12. A process of claim 1 further comprising the step of adding propane and butane to dephenolized kernel for extraction of oil.

13. A process of claim 1 further comprising the steps of adding alkaline solution to dissolve the pulp derived from oil extraction, centrifugation, protein precipitation, bleaching and spray drying to yield protein.

14. A process of claim 13, wherein after centrifugation and before spray drying, proteolytic enzyme is added for hydrolyzation to yield hydrolyzed protein.

15. A process of claim 1 further comprising the step of treating protein waste solution and waste solution from hydrolyzation of gossypol complex by evaporation and filtration, addition of saturated limewater, filtration and electrolysis of residual gossypol and condensation of residual solution to yield carbohydrates.

16. A process of any one of the preceding claims, wherein protein waste water and waste water from hydrolyzation are treated to recover useful components such as ethanol and water-soluble protein.

17. A process of any one of the preceding claims, wherein the seed is selected from the group consisting of cotton seed, rubber seed, sunflower seed, safflower seed, peanut, flax seed, hemp seed, rape seed, poppy seed and any other suitable seed.

18. A seed oil obtained by the process as claimed in any one of the preceding claims.

19. An apparatus for producing the seed oil as claimed in claim 18, according to the process as claimed in any one of the preceding claims.

ABSTRACT

INTEGRATED PROCESS FOR SEPARATION OF OIL, PROTEIN, CARBOHYDRATES, SHELL AND MINOR TOXIC COMPONENTS FROM SEEDS

This invention relates to a method for the separation of oil, protein, carbohydrates, shell and minor toxic components from seeds. The oil seed is subjected to a dehulling process to separate out the hull and kernel and the dehulled oil seed is then compressed into flakes under low temperature. The oil seed is then dephenolized and undergo low temperature delintion. In addition, direct hydrolyzation of the oil-complex is carried out. This technology can be used to produce high quality oil and obtain hydrolyzed protein, thereby comprehensively utilizing the oil seed.

(The most illustrative figure is FIGURE 1.)

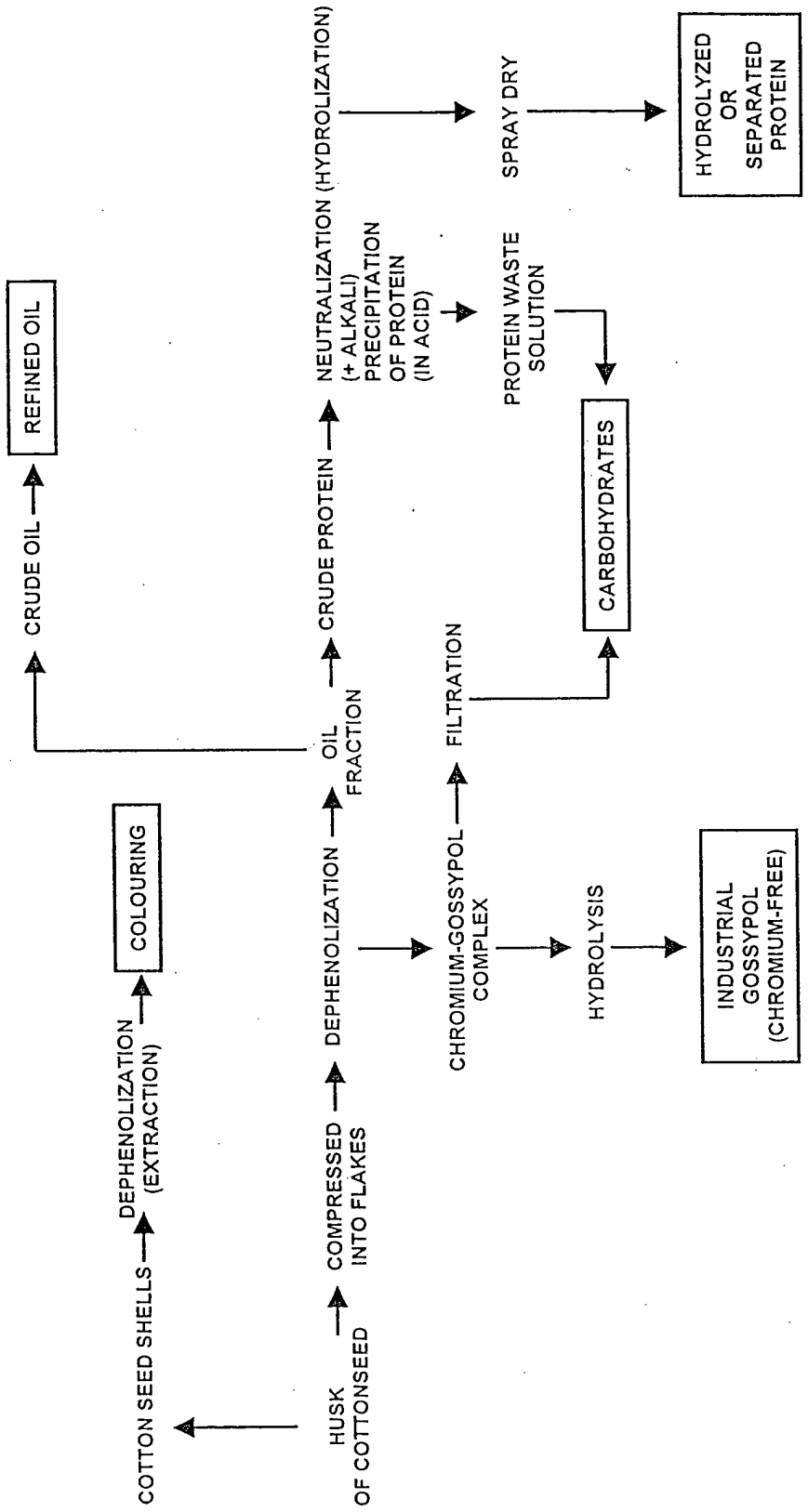
HUSK OF COTTONSEED
COTTON SEED SHELLS
COMPRESSED INTO FLAKES
DEPHENOLIZATION (EXTRACTION)
COLOURING
DEPHENOLIZATION
OIL FRACTION
CRUDE OIL
REFINED OIL
CRUDE PROTEIN
NEUTRALIZATION (HYDROLIZATION) (+ ALKALI) PRECIPITATION OF PROTEIN (IN ACID)
SPRAY DRY
HYDROLYZED OR SEPARATED PROTEIN
PROTEIN WASTE SOLUTION
CHROMIUM-GOSSYPOL COMPLEX
FILTRATION
CARBOHYDRATES
HYDROLYSIS
INDUSTRIAL GOSSYPOL (CHROMIUM-FREE)

FIGURE 1

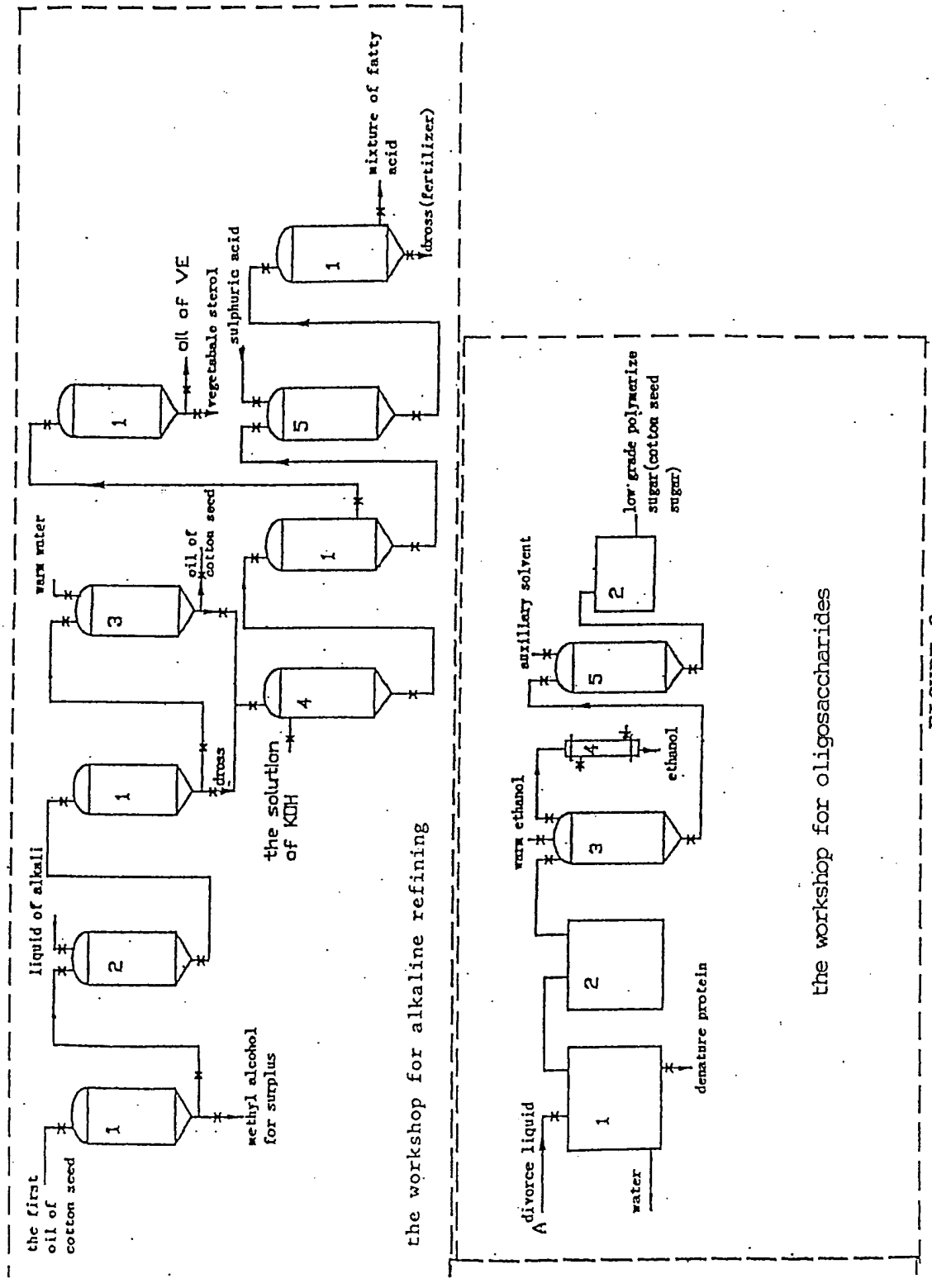
the first oil of cotton seed
methyl alcohol for surplus
liquid of alkali
dross
the solution of KOH
warm water
oil of cotton seed
oil of VE
vegetabale sterol
sulphuric acid
mixture of fatty acid
dross(fertilizer)
the workshop for alkaline refining
divorce liquid
water
denature protein
warm ethanol
ethanol
auxiliary solvent
low grade polymerize sugar(cotton seed sugar)
the workshop for oligosaccharides

FIGURE 2

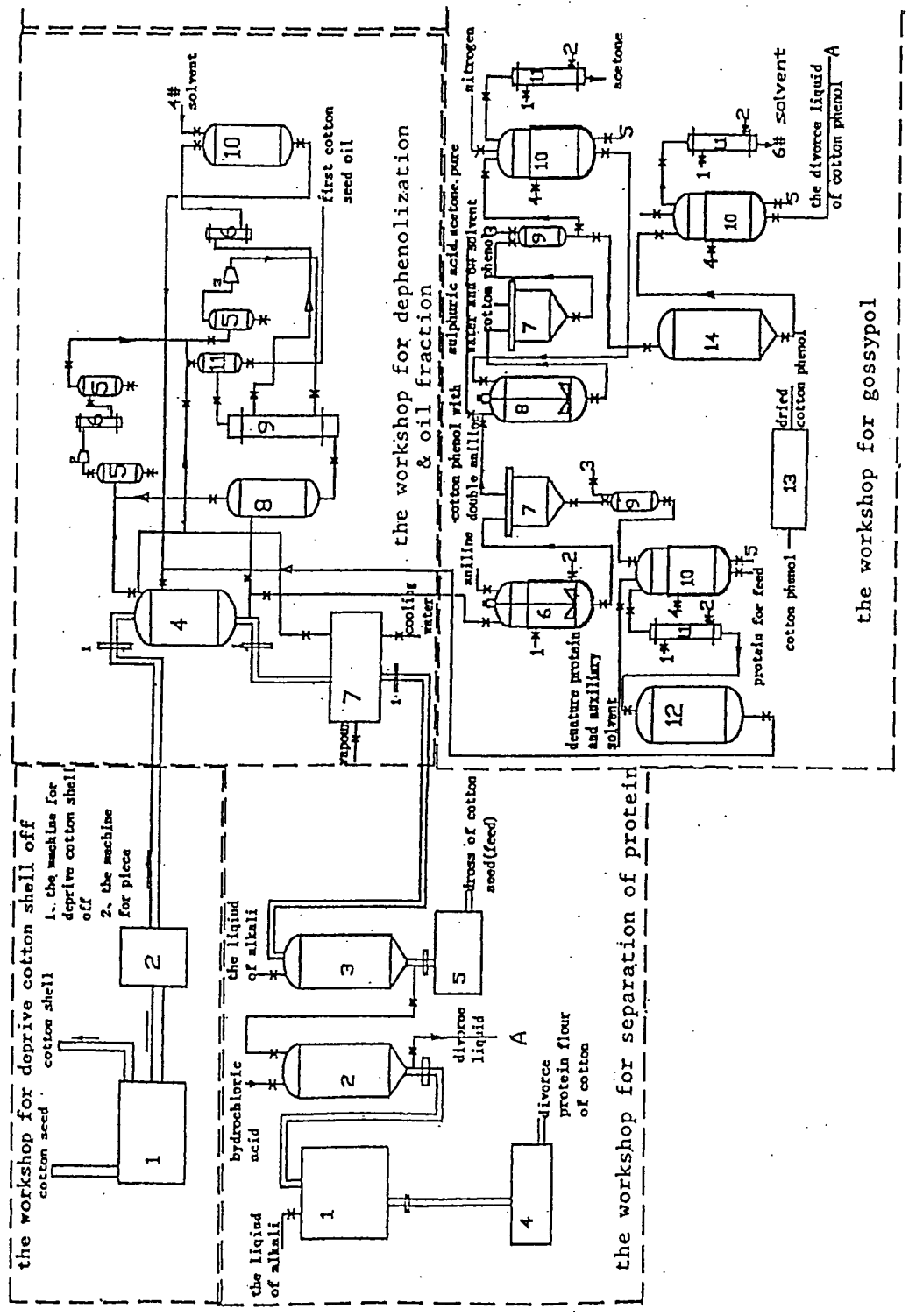
the workshop for deprive cotton shell off
cotton seed
cotton shell
1. the machine for deprive cotton shell off
2. the machine for piece
the liquid of alkali
hydrochloric acid
divorce liquid
A
divorce protein flour of cotton
mass of cotton seed(feed)
the workshop for dephenolization & oil fraction
4# solvent
first cotton seed oil
vapour
cooling water
sulfuric acid
acetone
nitrogen
acetone
water and oil solvent
cotton phenol
cotton phenol with double sulfuric acid
sulfuric acid
denature protein and auxiliary solvent
protein for feed
cotton phenol
dried cotton phenol
6# solvent
the divorce liquid of cotton phenol
A
the workshop for gossypol

FIGURE 3